

Determination of Inorganic and Organotin
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Atomic Absorption Spectrometry
(Journal Version)

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Determination of Inorganic and Organotin Compounds in Sea Water by Graphite Furnace Atomic Absorption Spectrometry*†

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Inorganic tin and organotin compounds in artificial sea water were determined at sub-p.p.b. levels. These compounds are separated from matrix elements in aqueous solutions by benzene extraction of their iodide forms from a 2 M sulphuric acid - 1.5 M sodium iodide solution containing 1% *m/V* ascorbic acid. The organic phase was partially vaporised to pre-concentrate the analytes and was injected directly into the treated graphite tube; the signal was measured by a Zeeman atomic absorption spectrometer. Using a matrix modifier, inorganic tin could be directly determined at sub-p.p.m. levels in the presence of organotin compounds.

Keywords: *Electrothermal atomisation atomic absorption spectrometry; matrix modification; organotin compounds; sea water; Zeeman background correction*

The very first application of a dialkyl substituted organotin compound as a heat stabiliser in poly(vinyl chloride) films was reported in 1940.¹ However, today such compounds are employed in a variety of industrial and agricultural applications, such as antioxidants and anticracking agents in rubber, as stabilisers for various polymers, as catalysts and as fungicides for agricultural products.²

The majority of organotin compounds used are of the R_2SnX_2 and R_4SnX type. Dibutyl- and dioctyl-tin compounds are used as catalysts and stabilisers for poly(vinyl chloride).³ The R_4SnX type also exhibits fungicidal activity.⁴ Tributyltin compounds are used as wood preservers⁵ and anti-fouling agents in paints for the hulls of ships.⁶ Triphenyltin, tripropyltin and tricyclohexyltin compounds are used mainly as pesticides in agriculture. These compounds are all toxic, and when released into the environment, pollution becomes a serious problem. For example, it is known that tributyltin inhibits development of oyster larvae⁷; also various methyl- and butyltin compounds at the parts per billion and lower levels are lethal to fish, crustaceans and molluscs.⁸

Organotin compounds are present in sea water at concentrations varying from 0.05 to 0.5 p.p.b. The high toxicity together with low concentrations of these compounds present in the environment has prompted the search for extremely sensitive analytical methods. Spectrophotometric methods have been used to measure inorganic tin at low concentrations. A number of colorimetric reagents, such as dithiol,^{9,10} phenylfluorene,¹¹⁻¹⁶ pyrocatechol violet^{15,17} and 8-hydroxyquinolinol (oxine),^{18,19} have been used. These reagents lack sensitivity and selectivity with detection limits in the 0.02–10 µg range. Flame atomic absorption spectrometry has been used with detection limits for tin at parts per million levels.²⁰⁻²² Using the carbon rod, Everett and West²³ reported the atomic absorption spectrometric determination of tin as a wear metal in oils at 5–20 ng levels. Meranger²⁴ has described a method to determine tin in alcoholic beverages using a graphite furnace technique with a detection limit of 0.04 p.p.m.

Organotin compounds have been determined using various methods. These include colorimetry,²⁵⁻³⁰ flame atomic absorption spectrometry, FAAS,³¹⁻³⁷ electrothermal atomisation atomic absorption spectrometry (ETA-AAS),³⁷⁻⁴² polarography,⁴³⁻⁴⁷ gas chromatography (GC)⁴⁸⁻⁵⁵ and high-performance liquid chromatography (HPLC).⁵⁶ The hydride

generation (HG) procedure followed by trap collection with a separation based on boiling-points together with FAAS,^{34,57-61} ETA-AAS^{62,63} or flame photometric detection (FPD)⁶⁴⁻⁶⁶ has been employed to speciate and determine inorganic tin and organotin compounds in aquatic environments. Other hybrid techniques have included: ion-exchange HPLC-ETA-AAS⁶⁷ for di- and tributyltins in water; HPLC-ETA-AAS⁶⁸ for organotin in water; GC-FAAS⁶⁹ for inorganic tin and methyltin in water; GC-FPD^{60,70} for inorganic tin and organotin in sediments and sewage sludge samples; HG-GC-quadrupole mass spectrometry⁷¹ for methyltins in sediments; HPLC-HG-d.c. plasma emission spectrometry⁷² for methylated organotins in food and sea water; and HPLC-FAAS⁷³ for organotin in natural waters.

Direct determination of inorganic tin and organotin compounds in sea water has not been successful because of matrix effects, *i.e.*, foreign ions present at higher concentrations. To facilitate the determination, a separation technique prior to analysis must be employed. Ion-exchange techniques have been used to separate and concentrate inorganic tin⁷⁴⁻⁷⁶ and organotin compounds.^{31,33,77-79} An alternative method is extraction of tin compounds into a non-polar solvent such as benzene or toluene. Extraction of inorganic tin into these solvents as tin iodide from a sulphuric acid - potassium iodide solution has been developed into a quantitative, selective and sensitive method based on both spectrophotometric⁸⁰⁻⁸² and flame atomic absorption spectrometric detection.⁸²⁻⁸⁴ The papers dealing with extraction of organotin compounds involved benzene extraction of organotins into HCl-NaCl media⁵³ and dichloromethane extraction of phenyl derivatives of tin⁵⁵ and of butyltin compounds in natural waters.⁶²

Most of the techniques employed in the determination of organotin compounds use hydride generation with AA, gas chromatography or hybrid techniques and benefit from the high sensitivity together with the ability to speciate different compounds. However, they lack simplicity because optimisation of the different parameters and setting up the apparatus are elaborate. The present technique, although confined to the determination of total organotin compounds, benefits from high sensitivity, good precision and the simplicity of the procedure.

In this work, inorganic tin and organotin compounds in artificial sea water were extracted into benzene from a solution of 3 M H_2SO_4 - 1.5 M NaI, 1% *m/V* ascorbic acid. The organic phase was separated and after adequate vaporisation, it was injected directly into a treated graphite furnace and the atomic absorption signal was measured. One of the problems encountered in the determination of tin with graphite furnace atomic absorption is the formation of difficult to atomise tin carbide with the concomitant loss of sensitivity. It has been found that treatment of the graphite furnace with refractory

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† This paper is dedicated to the memory of Professor John M. Ottaway.

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metals improved the atomisation efficiency resulting in an increased sensitivity and a lowering of the interference effects for tin and some other elements.⁸⁶⁻⁹¹ In order to take advantage of the higher sensitivity of the graphite furnace relative to that for flames, the graphite tubes were treated with different refractory elements and the results were compared.

Experimental

Reagents

De-ionised water was used in all the experiments. All glassware used for preparation, storage and dilutions was cleaned by soaking in 10% V/V HCl followed by rinsing with de-ionised water. All compounds used in the experiments were of analytical-reagent grade. Laboratory-reagent grade solvents were used throughout.

Standards

All tin compounds were purchased from Alfa Chemical (Danvers, MA, USA). Stock solutions (1000 p.p.m.) of methyltin and butyltin chlorides were prepared in 10% V/V HCl with de-ionised water and methanol, respectively. Working standards were freshly prepared with de-ionised water prior to analysis. Artificial sea water of 35‰ salinity was prepared from the appropriate salts with the composition⁹² given in Table 1.

Apparatus

A Hitachi 180-80 polarised Zeeman graphite furnace atomic absorption spectrometer (Hitachi, Tokyo, Japan) was used for this study. The outer gas (Ar) was maintained at a flow-rate of 3 l min⁻¹ and the carrier gas (Ar) at a flow-rate of 0.2 l min⁻¹; the interrupted mode was used during atomisation. The tin hollow-cathode lamp was operated at 10 mA. All measurements were made at the 224.6-nm resonance line with a spectrometer band width of 0.4 nm. Peak area was used for all measurements, and signals were recorded on the printer as well as the strip chart recorder allowing the simultaneous measurement of signal and background absorption. Sample solutions were introduced into the graphite furnace in both 10-

and 50- μ l aliquots for aqueous solutions and in 50- μ l aliquots for organic solutions.

Graphite Surface Treatment

Aqueous solutions 5-10% m/V of Mo, W, Ta, Ti, Zr, V, Nb and Hf were prepared for use in the surface treatment. The graphite tubes were soaked overnight in the appropriate solutions, then dried at 120°C for 4 h. The impregnated tubes were dried inside the furnace for 60 s at 120°C, 60 s at 400°C, 30 s from 400-1000°C, 30 s from 1000-2500°C, 10 s from 2500-2700°C and kept at 2700°C for 10 s, with the interrupted mode for the final stage. This heating cycle was repeated twice.

Treatment and Type of Furnace Tube

In order to investigate the effectiveness of the surface treatment, aqueous solutions of SnCl₄ were injected into the tubes. The solution was dried at 80-120°C for 20 s, ashed at 400°C for 20 s and atomised at 2700°C for 7 s. For comparison, a tantalum tube and also tungsten-lined graphite tubes were employed. The sensitivity for Sn (as SnCl₄) with and without gas flow are given in Table 2. The results show an over-all improved sensitivity of 3-5 times for the impregnated tube and a further increase in sensitivity when the gas-interrupted mode was used. The Mo-, Ta-, Zr- and W-treated tubes were further employed for investigations of long-term stability and precision. Excellent precision was obtained for W- and Zr-treated tubes, with the best precision being for the Zr-treated tubes. However, the W-treated tubes proved to have superior lifetimes [(Na₂WO₄ compared with Zr(SO₄)₂]. Therefore, W-treated tubes were used for all subsequent experiments.

Direct Determination of Inorganic Tin and Organotin in De-ionised and Artificial Sea Water

During the course of the experiments, it was noticed that ramp atomisation increased the sensitivity by about 50% at moderate absorbance values and even more at greater absorbance values. Using an optimised 25-s ramp atomisation, analytical calibration graphs for aqueous solutions of inorganic tin and organotin compounds are given for injection volumes of 50 μ l in Fig. 1. The calibration graphs resembled each other except for tributyltin, which has a smaller slope giving rise to lower sensitivity and poorer detection limits, as has been reported by other workers.^{34,60} Table 3 summarises the analytical figures of merit for inorganic tin and organotin compounds in aqueous solutions.

For comparison, standard solutions of SnI₄ in benzene were prepared from the 1000 p.p.m. stock solution of tin iodide in

Table 1. Composition of artificial sea water

Salt	Concentration	
	mol kg ⁻¹	g kg ⁻¹ of solution
NaCl	0.42664	24.001
Na ₂ SO ₄	0.02926	4.011
KCl	0.01058	0.761
CaCl ₂	0.01077	1.153
MgCl ₂	0.05518	5.069

Table 2. Comparison of sensitivity and relative standard deviations for the determination of tin (as SnCl₄) with metal-treated, metal and metal-lined tubes

Type of tube	Sensitivity*	Sensitivity	RSD, %
	with gas flow/ μ g	with gas stop/ μ g	
Untreated graphite	5600	91	—
Hf treated	2600	—	—
Mo treated	1300	37	5.7
Nb treated	1700	—	—
Ta treated	1400	33	7.5
Ti treated	2000	—	—
V treated	2100	—	—
W treated	1400	29	4.3
Zr treated	1300	28	3.6
W-lined tube	1500	36.5	—
Ta tube	1600	45	—

* Concentration which gives an absorbance of 0.0044.

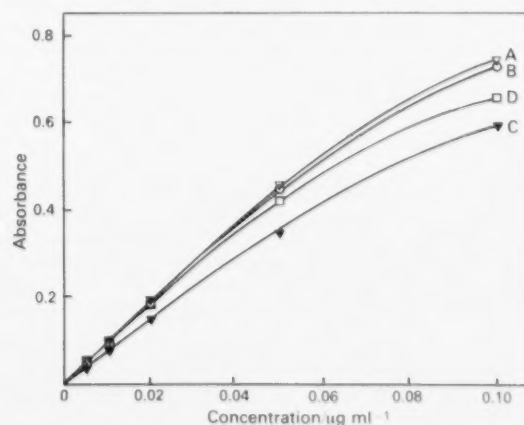


Fig. 1. Analytical calibration graphs for SnCl₄ (A), CH₃SnCl₃ (B) and (C₄H₉)₃SnCl (C) in de-ionised water and SnI₄ in benzene (D)

Table 3. Analytical figures of merit for aqueous solutions of inorganic tin and organotin compounds with 10- and 50- μ l sample aliquots

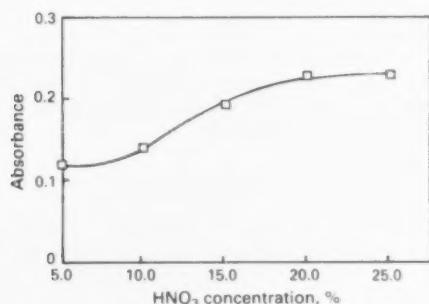
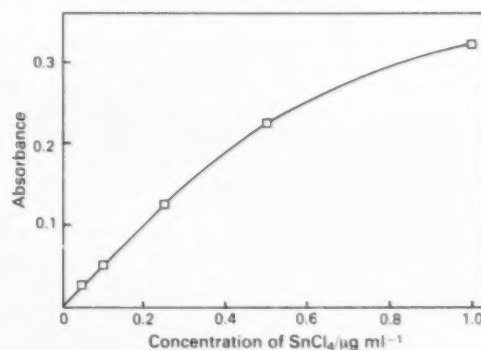
Compound	Linear range, p.p.b.		Sensitivity, p.p.b.		Detection limit,* p.p.b.		RSD,† %	
	10 μ l	50 μ l	10 μ l	50 μ l	10 μ l	50 μ l	10 μ l	50 μ l
SnCl ₄	2.5–100.0	0.60–45.00	1.9	0.45	2.5	0.60	3.8	4.3
CH ₃ SnCl ₃	2.8–100.0	0.65–40.00	2.2	0.50	2.8	0.65	4.0	4.5
(CH ₃) ₂ SnCl ₂	2.8–100.0	0.65–40.00	2.2	0.50	2.8	0.65	4.0	4.5
(CH ₃) ₃ SnCl	2.8–100.0	0.65–40.00	2.3	0.52	2.8	0.65	4.0	4.7
C ₄ H ₉ SnCl ₃	2.8–100.0	0.65–40.00	2.3	0.52	2.8	0.65	4.0	4.7
(C ₄ H ₉) ₂ SnCl ₂	2.8–100.0	0.65–40.00	2.3	0.52	2.8	0.65	4.2	4.7
(C ₄ H ₉) ₃ SnCl	4.5–100.0	1.00–40.00	3.5	0.75	4.5	1.00	4.3	5.0
SnI ₄ in benzene	—	0.65–45.00	—	0.50	—	0.65	—	4.2

* Based on concentration of blank giving a signal 3 $\times$ standard deviation.

† Relative standard deviation (%) for seven replicate determinations at concentrations that are ten times the detection limits.

Table 4. Analytical figures of merit for inorganic tin and organotin chlorides extracted into benzene

Compound	Linear range		Sensitivity		Detection limit		RSD, %
	ng ml ⁻¹	ng	ng ml ⁻¹	ng	ng ml ⁻¹	ng	
SnCl ₄	0.020–0.400	0.26–5.00	0.0065	0.085	0.020	0.26	4.8
CH ₃ SnCl ₃	0.020–0.350	0.25–4.40	0.0064	0.083	0.020	0.25	5.0
(CH ₃) ₂ SnCl ₂	0.023–0.350	0.28–4.40	0.0070	0.090	0.023	0.28	5.3
(CH ₃) ₃ SnCl	0.023–0.350	0.28–4.40	0.0070	0.090	0.023	0.28	5.5
C ₄ H ₉ SnCl ₃	0.020–0.300	0.25–3.80	0.0060	0.080	0.020	0.25	5.5
(C ₄ H ₉) ₂ SnCl ₂	0.016–0.300	0.20–3.80	0.0050	0.065	0.016	0.20	5.7
(C ₄ H ₉) ₃ SnCl	0.020–0.300	0.25–3.80	0.0060	0.080	0.020	0.25	6.0

**Fig. 2.** Effect of HNO₃ concentration on the atomic absorption signals for SnCl₄ in artificial sea water**Fig. 3.** Analytical calibration graphs for SnCl₄ in artificial sea water

benzene and measured as before using 50- μ l sample aliquots. The calibration graph is given in Fig. 1, and the data are summarised in Table 4.

Attempts were made to measure tin directly in sea-water media. Even with optimised conditions, there was no measurable signal above a very high background. Different matrix modifiers, including ammonium nitrate, nitric acid, sucrose, ascorbic acid and oxalic acid, were all evaluated, of which only nitric acid resulted in a low background absorption. The effect of acid concentration on the tin (as SnCl₄) absorption signal is shown in Fig. 2; a 25% V/V solution of nitric acid seemed to be optimal. To provide an even higher sensitivity, sample volumes ranging from 10 to 50 μ l were injected in the tube but little improvements occurred as a result of the very high concentration of the matrix elements. All succeeding experiments were therefore confined to sample volumes of 10 μ l. The calibration graph for tin (as SnCl₄) in artificial sea water is given in Fig. 3. It is concluded that inorganic tin could be determined in sea water with a sensitivity and detection limit of 9.5 and 11.5 p.p.b., respectively, which is poorer by a factor of five when compared with determinations in de-ionised water. The RSD for the determinations was 3.8%. Organotin compounds were also examined, but there was no measurable signal at levels of 0.1 p.p.m. Although addition of nitric acid

reduced the background absorption, no measurable signal was obtained. Therefore, it is possible to measure inorganic tin in the presence of organotin in sea water containing 25% nitric acid. Oxalic and salicylic acid modifiers resulted in an increase in the absorption signal by 30 and 60%, respectively, for organotin compounds; however, the background absorption was still too high to measure organotin at the concentration levels present in sea water.

Extraction of Inorganic Tin and Organotin Compounds

To 250 ml of artificial sea water spiked with 0.25 ml of a 1 p.p.m. solution of an appropriate tin compound and held in a 500-ml separating funnel, 3 g of ascorbic acid, 50 ml of concentrated sulphuric acid and 50 ml of freshly prepared 150% m/V sodium iodide solution were added. The final solution was 1 p.p.b. in tin, 1% m/V in ascorbic acid, 3 M in H₂SO₄ and 1.5 M in NaI. To the contents of the funnel, 30 ml of benzene were added and shaken for about 2 min. Several minutes were allowed for the layers to separate, and then the lower aqueous layer was transferred into a second funnel and another 30 ml of benzene were added to this second funnel and the extraction procedure was repeated. The organic layers

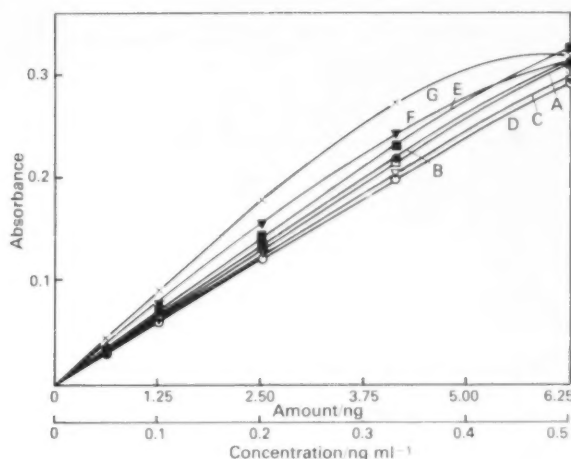


Fig. 4. Analytical calibration graphs for the benzene extraction of SnCl_4 (A), CH_3SnCl_3 (B), $(\text{CH}_3)_2\text{SnCl}_2$ (C), $(\text{CH}_3)_3\text{SnCl}$ (D), $\text{C}_4\text{H}_9\text{SnCl}_3$ (E), $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$ (F) and $(\text{C}_4\text{H}_9)_3\text{SnCl}$ (G) from artificial sea water

were combined in a beaker, kept warm on a hot-plate and evaporated to about 0.5 ml under a strong stream of air. Appropriate dilutions of this solution with benzene allowed the construction of a calibration graph using 50- μl aliquots at the optimised conditions. The same procedure was applied to the blank. The analytical calibration graphs for the extracted inorganic tin and organotin compounds in benzene are given in Fig. 4. Table 4 shows the analytical figures of merit obtained by this method. By comparing the analytical figures of merit for the direct measurement of tin in benzene with those obtained after the extraction procedure, an average pre-concentration factor of 76 was obtained for the extraction procedure. Because the analytical calibration graphs for the aqueous and organic media resemble each other for inorganic tin and because the calibration graph for the organotin compounds are almost identical with those for inorganic tin in de-ionised water, the pre-concentration factors given in Table 5 were obtained by comparing the analytical figures for organotin in de-ionised water with those obtained after extraction. Although there was no sea water with unknown tin contents available to examine the usefulness of the extraction technique, replicate extractions and subsequent measurements of inorganic tin and organotin compounds resulted in highly consistent calibration graphs, i.e., the slopes of all the graphs were within 95% of the average slope. Benzene was superior to other organic solvents, such as carbon tetrachloride, carbon disulphide and hexane, in terms of extraction efficiency and AA sensitivity and selectivity.

Separating Tin(IV) from Sea Water Prior to Extraction

In the separation of inorganic tin from other compounds, 250 ml of artificial sea water spiked with 0.25 ml of the 1 p.p.m. tin(IV) standard solution and 1.5 ml of 1 M NaOH were taken; the solution was stirred for 1 h, and the resulting milky precipitate was allowed to settle overnight.⁹³ The supernatant liquid was decanted, and the precipitate was dissolved in a few drops of concentrated hydrochloric acid. In order to compare the recovery of inorganic tin from sea water with the previous extraction procedure for sea water, the dissolved precipitate was added back to 250 ml of artificial sea water. The tin in this solution was then extracted by the previous benzene procedure. The tin recovery in this instance was within 95% of the tin measured by the previous benzene extraction procedure.

Table 5. Measured pre-concentration factors for tin compounds

Compound	Pre-concentration factor
SnCl_4	76.0
CH_3SnCl_3	78.0
$(\text{CH}_3)_2\text{SnCl}_2$	71.5
$(\text{CH}_3)_3\text{SnCl}$	72.5
$\text{C}_4\text{H}_9\text{SnCl}_3$	86.5
$(\text{C}_4\text{H}_9)_2\text{SnCl}_2$	100.0
$(\text{C}_4\text{H}_9)_3\text{SnCl}$	117.0

Recovery of Inorganic Tin and Organotin Compounds

Recovery tests were conducted on the artificial sea water to which had been added 150 ng of SnCl_4 and different organotin compounds, and the same analytical procedure was applied to the determination of 150 ng of the individual compounds. Average recoveries were found to be 100% and 95–104% for the inorganic tin and the different organotin compounds, respectively.

Conclusions

The results reported in this paper show that it is possible to apply the extraction technique in order to separate, and concentrate, inorganic tin and organotin compounds in sea water from the large amounts of interfering elements and measure them at the sub-p.p.b. level by graphite furnace atomic absorption spectrometry. It is also possible to determine inorganic tin by co-precipitating tin with partial precipitation of calcium and magnesium, hence to measure the total organic tin in sea water. Direct determination of inorganic tin in sea water at the sub-p.p.m. level is also possible by use of 25% V/V solutions of nitric acid.

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